

Fluidizable Catalysts for Hydrogen Production from Biomass Pyrolysis/Steam Reforming

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Objectives

- Develop attrition resistant supports and multi-functional, multi-component fluidizable catalysts from these supports for efficiently reforming pyrolysis vapors and liquids derived from biomass.
- Develop fluidizable catalysts for reforming feedstocks derived from post-consumer waste (trap grease, waste plastics).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology
- Z. Catalysts

Approach

- Develop and optimize fluidizable reforming catalysts using CoorsTek, Inc. specialty aluminas as supports.
- Evaluate catalytic reforming performance with gas and liquid phase feedstocks derived from biomass and post-consumer wastes.
- Design and fabricate a micro-scale reactor for rapid screening of catalysts.

Accomplishments

- Optimized catalyst composition for reforming the aqueous fraction of liquids derived from biomass pyrolysis.
- Developed a catalyst for waste grease reforming.
- Designed and fabricated a rapid catalyst test system.

Future Directions

- Develop catalysts for other renewable feedstocks.
- Improve support materials for bubbling and circulating bed systems.
- Understand and overcome deactivation mechanisms (coking, sulfur and phosphorous poisoning).
- Develop non-nickel reforming catalysts.

Introduction

Commercial naphtha reforming catalysts are used to process heavy crude oils in packed bed configurations, and they are the most likely industrial catalysts available for reforming biomass-derived pyrolysis liquids. These catalysts cannot withstand the harsh reaction conditions used in a fluidized bed for producing hydrogen from pyrolysis liquids. Fluidization is preferred in such a case to optimize the contact of catalyst with the feedstock and minimize coke formation. In a typical commercial fixed bed reactor, the pyrolysis liquids tend to form coke instead of being reformed. The commercial backed bed catalysts, which generally consist of nickel coated onto alumina supports, attrit significantly when fluidized and yield consistent losses of 10-20 wt% per day. Because process economics cannot tolerate such catalyst loss, we needed to identify and/or develop an attrition-resistant support that can withstand fluidized reforming conditions.

Numerous support screening experiments showed that commercially available specialty alumina materials produced by CoorsTek Ceramics could have the necessary strength to withstand fluidizing conditions. Catalysts made from these supports have been used to reform pyrolysis liquids, and the generated performance data have been used to refine subsequent catalyst compositions. This year we report results from continued development of catalysts for reforming aqueous pyrolysis liquids and preliminary results from testing our catalysts with other renewable feedstocks including biomass gasification vapors and waste trap grease. These feedstocks require fine-tuning of the catalyst composition to handle sulfur impurities in trap grease and tars contained in gasification vapors. The challenge now is to design novel catalysts with improved reforming activity, gasification activity (gasify coke deposits on the catalyst surface), and poison tolerance (sulfur and phosphorous contained in trap grease) for these new feedstocks.

Approach

We have developed robust nickel-based reforming catalysts from strong alumina particles produced by CoorsTek Ceramics. These materials,

which can withstand the harsh conditions required for reforming pyrolysis liquids, produce hydrogen with efficiencies as good or better than those of the best commercial catalysts. Our best original catalyst composition, compared to the composition of a commercial reforming catalyst, provided good activity and performance for reforming aqueous pyrolysis liquids. Our work this year focused on refining that base composition to further improve catalyst performance for reforming the liquids. Additionally, we began testing the basic catalyst with other renewable feedstocks and assessing how feedstock changes impact catalyst performance. The overall goal is to design cost efficient feedstock-flexible reforming catalysts.

All catalysts were evaluated with the aqueous fraction of pyrolysis oils from pine or mixed hardwoods for a 24-hour period in a two-inch fluidized bed laboratory scale reactor equipped with in-line gas analyzers and process controllers. Inlet and outlet gas compositions at steady state conditions were used to calculate hydrogen, carbon dioxide, carbon monoxide, and methane yields. We used the CO_2/CO ratio (from the reformed gas mixture) as a general measure of selectivity for water-gas shift (WGS) and coke gasification, and we used the H_2/CH_4 ratio to measure reforming selectivity. Overall activity is measured by the H_2 yield, which is the ratio of actual yield to theoretical yield $\times 100$. Theoretical yield is the amount of hydrogen produced if reforming and WGS reactions convert all carbon in the feedstock to CO_2 . Performance data were then correlated with catalyst compositions to guide the next choice of catalyst "recipe" to test.

Results

Table 1 shows catalyst and performance data for four catalyst compositions compared to the commercial reforming catalyst C 11 NK. Our goal this year was to improve hydrogen yields (reforming activity) and to improve feeding of the pyrolysis liquids into the fluidized catalyst bed. The H_2/CH_4 ratio shows that we can meet or exceed commercial catalyst selectivity for hydrogen production though WGS performance, measured by CO_2/CO , is still less than that of the commercial material. Note as well that our catalysts use significantly smaller quantities of Ni, Mg, and K than does the

commercial material. The implication of this result is that we can now consider using other reforming metals like platinum and palladium since required amounts are less.

Figure 1 compares performance data for several catalysts and lists the composition data. Catalysts 10-12 all contain about the same amount of potassium oxide (K_2O), and feeding upsets are clearly seen as spikes in the hydrogen content. We think the spikes are caused by solid chunks of feedstock, located at the injection nozzle, breaking up in the fluidized catalyst bed. The commercial catalyst and catalysts 14-15 do not exhibit feedstock spiking, and we think this is attributable to the increased amount of K_2O contained in these materials. Potassium promotes gasification, the

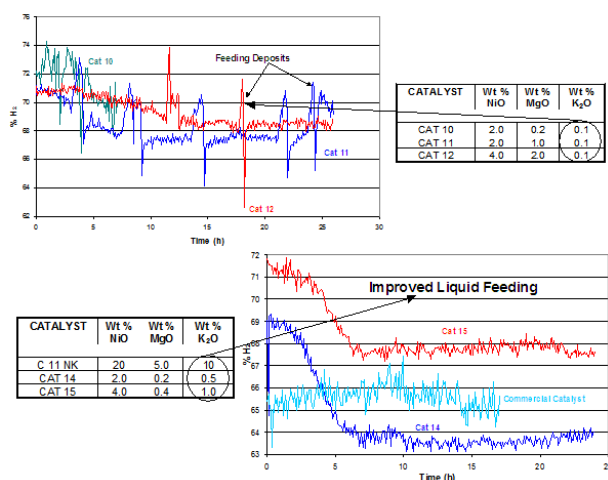


Figure 1. Catalyst Performance for H_2 Production from Reforming Aqueous Pyrolysis Liquids at $850^\circ C$ in a 2-inch Fluidized Bed Reactor; Feeding Deposits Are Related to Catalyst K_2O Content

formation of volatile carbon oxides from solid carbon, and seems to inhibit the formation of carbonized feedstock chunks at the injection nozzle. Improving feeding behavior of a complex, difficult to feed material is a significant accomplishment that will allow routine use of aqueous pyrolysis liquids in fluidized reactors.

Figure 2 compares performance of one of our best catalysts with that of the commercial material for pyrolysis liquid reforming. Our catalyst produces hydrogen in higher yield than the commercial catalyst though our WGS activity is lower. Our catalyst also produces more methane though the commercial catalyst likely reaches the same methane concentration for extended reaction time. The WGS reaction, which produces H_2 and CO from catalytic reaction of H_2O and CO_2 , is also catalyzed by nickel.

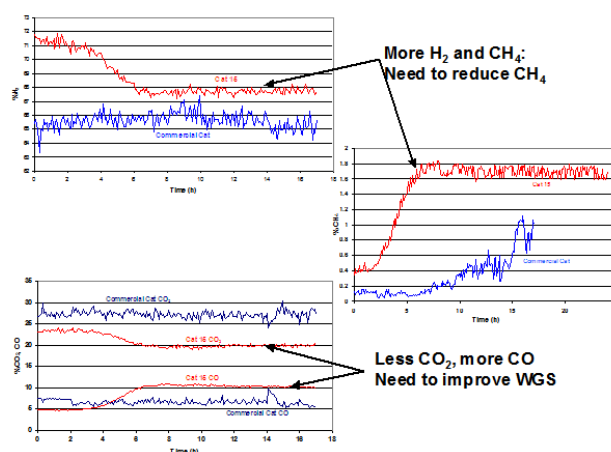


Figure 2. Catalyst Performance of our Catalyst #15 and the Commercial Catalyst C 11 NK for Pyrolysis Liquid Reforming at $850^\circ C$ in a 2-inch Fluidized Bed Reactor

Table 1. Catalyst Selectivity Data for Reforming Aqueous Pyrolysis Oil Extracts Calculated During the Interval 20-23 Hours of On-Stream Reaction

CATALYST	Wt % NiO	Wt % MgO	Wt % K_2O	SUPPORT % Al_2O_3	CO_2/CO	H_2/CH_4	H_2 YIELD
C 11 NK	20	5.0	8.0	MIX	4.1	39.6	91
CAT 11	2.0	1.0	0.1	90	1.4	54.0	84
CAT 12	4.0	2.0	0.1	90	1.8	57.1	87
CAT 14	2.0	0.2	0.5	90	1.0	30.0	79
CAT 15	4.0	0.4	1.0	90	2.1	39.9	83

We continue to work on improving WGS activity through composition changes.

We evaluated the performance of catalyst 15 with two feedstocks: pyrolysis liquids and liquid trap grease (waste restaurant grease). The trap grease was washed with several volumes of hot water to remove soluble impurities like sodium chloride prior to use. The trap grease is less chemically complex than the pyrolysis liquids and should be easier to reform. Figure 3 verifies that assumption by showing a slightly better hydrogen yield from trap grease. Initial WGS activity was better for trap grease, but it began to decline after three hours of reaction. WGS activity for pyrolysis liquids never reached that of trap grease though the decline came later at six hours of reaction and reached a steady state. Methane production was the same for both feedstocks. Preliminary surface analysis of the fresh and used catalysts (all composition 15) showed that trap grease catalyst contained about 150 ppm of surface phosphorous, which had to come from the feedstock as neither the fresh catalyst nor the catalyst used for pyrolysis liquids contained any phosphorous. It is possible that phosphorous impacted WGS activity

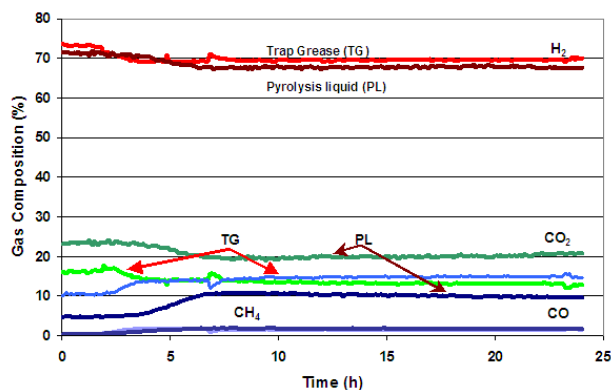


Figure 3. Catalyst #15 Performance Data for H₂ Production by Reforming Aqueous Pyrolysis Liquids and Waste Grease at 850°C in a 2-inch Fluidized Bed Reactor

though it did not appear to affect hydrogen production. This result demonstrates the impact that feedstock will have on overall reaction performance.

Conclusions

- Developed novel, attrition-resistant fluidizable reforming catalysts with CoorsTek Specialty Ceramics.
- Evaluated performance of 16 catalysts for 24 hrs with pyrolysis oil-derived feedstocks in a small pilot scale reactor. This provides steady state comparison of catalyst performance with different feedstocks and varied catalyst compositions.
- Improved reforming activity (compared to commercial catalyst) for pyrolysis oils with reduced nickel content catalysts though WGS activity remains slightly less than that of the commercial catalyst.
- Improved pyrolysis oil feeding to the fluidized catalyst bed by increasing potassium oxide (K₂O) content.
- Developing sulfur- and phosphorous-tolerant catalyst compositions for reforming waste grease.

FY 2003 Publications/Presentations

1. K. Magrini, SC. Czernik, R. French, Y. Parent, E. Chornet, "Fluidizable Catalyst Development for Steam Reforming Biomass-Derived Feedstocks", in preparation.

Special Recognitions & Awards/Patents Issued

1. Record of Invention on fluidizable catalysts filed with DOE.